

## Supplementary Information

### Metal-free Porous Phosphorus-Doped g-C<sub>3</sub>N<sub>4</sub> Photocatalyst Achieving

### Efficient Synthesis of Benzoin

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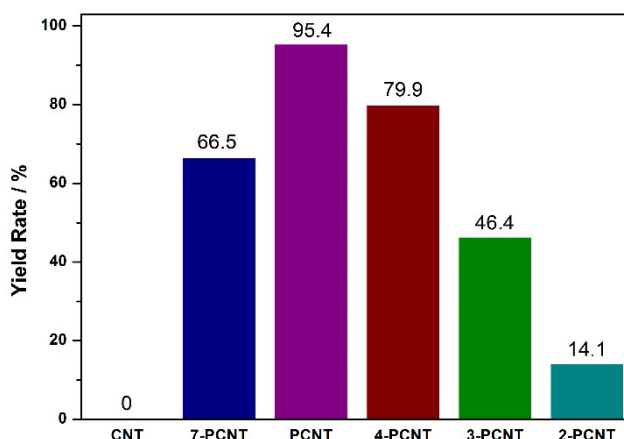
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## SUPPLEMENTARY EXPERIMENT DETAILS

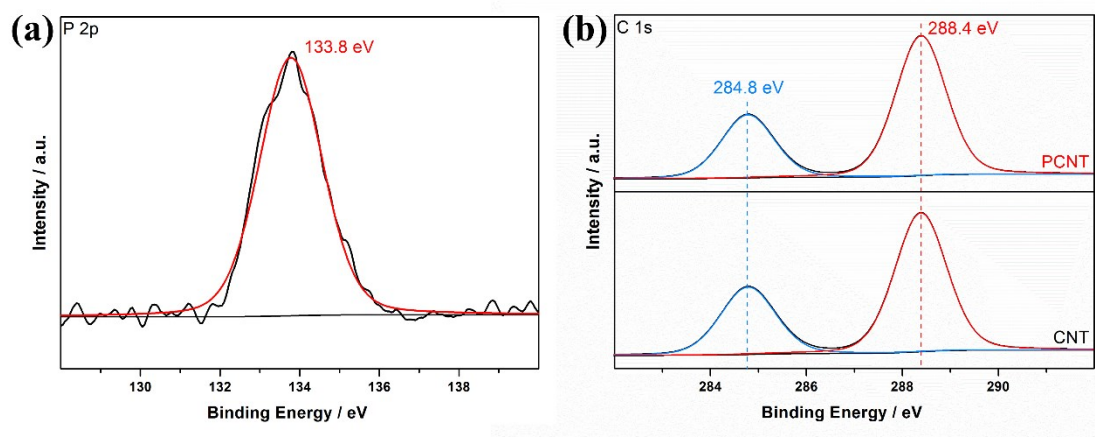
**Characterizations.** The X-ray diffraction (XRD) observation was conducted on a Philips X'Pert Pro Super diffractometer. The microstructures of catalysts were investigated through a FEI Sirion200 field emission scanning electron microscope (SEM) and a JEM-2100F transmission electron microscope (TEM), with energy-dispersive spectroscopy (EDS) mapping characterized on the same instrument. The Zeta potential was measured via Micromeritics NANOPLUS 3. X-ray photoelectron spectroscopy (XPS) was done on a VGESCALAB MK II spectrometer. N<sub>2</sub> adsorption isotherms were recorded from an ASAP 2020 M PLUS analyzer. The ultraviolet–visible (UV–vis) spectra were acquired from a Perkin Elmer Lambda950 spectrophotometer. Photoluminescence (PL) spectra were evaluated by an Edinburgh FLS920 fluorescence spectrometer. X-ray absorption near edge structure (XANES) spectra were executed in the National Synchrotron Radiation Laboratory (NSRL) in Hefei, China.

## SUPPLEMENTARY FIGURES

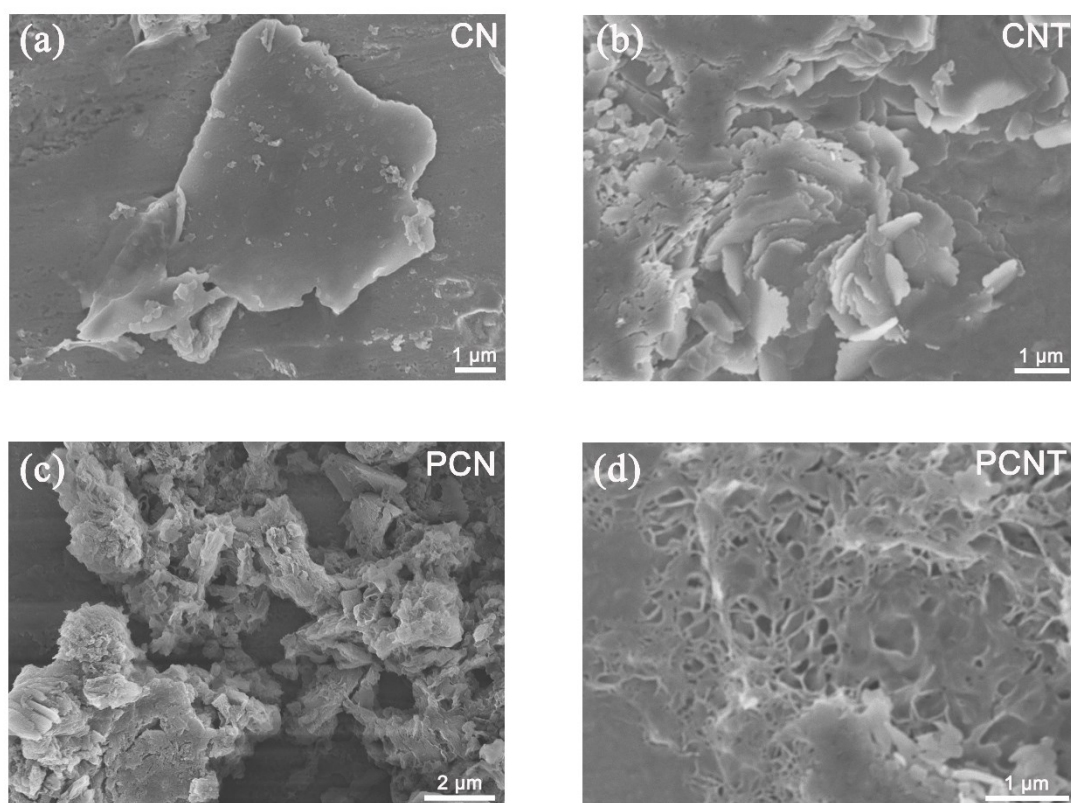


**Figure S1.** Yield rate of benzoin on PCNT with different phosphorus doping concentration within 6 h.

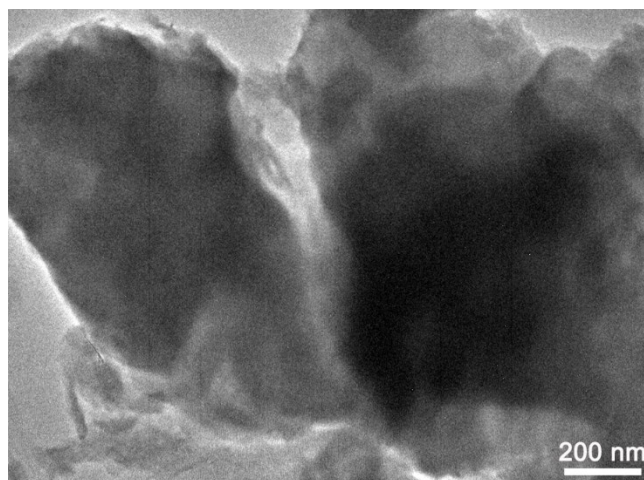
In order to determine the optimal doping content of phosphorus in PCNT for synthesis of benzoin, a series of PCNT, i.e., 7-PCNT, 4-PCNT, 3-PCNT and 2-PCNT were synthesized, following the same procedure as that of PCNT except that the mass ratio of 2-aminoethylphosphonic acid (AEP): melamine (ME) was changed to 1/70, 1/40, 1/30 and 1/20, respectively. Then the effect of mass ratio (AEP:ME) on the photocatalytic benzoin synthesis activity was investigated. As shown in Fig.S1, the highest yield rate of benzoin is 95.4%, which is achieved at the mass ratio of 1/60 (PCNT). On basis of the above result, PCNT with the optimal mass ratio (AEP:ME) of 1/60 was selected for investigation in this work.



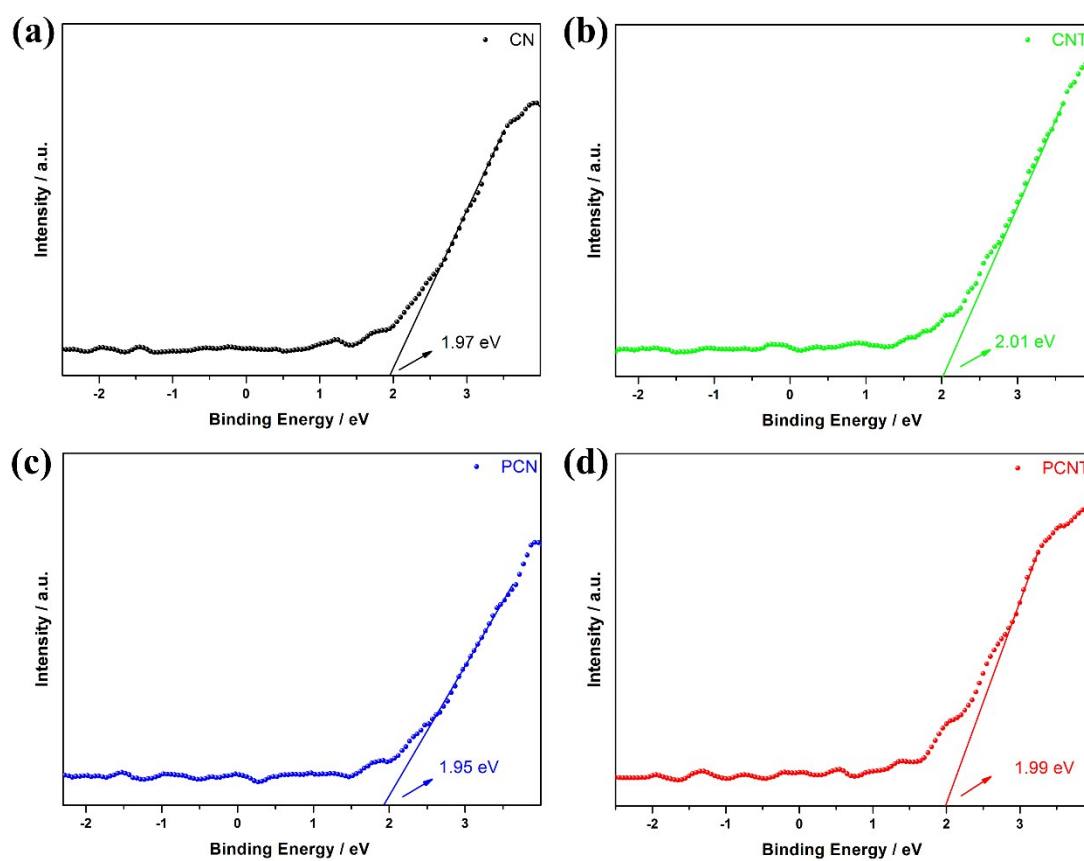
**Figure S2.** (a) XPS P 2p spectra of PCNT. (b) XPS C 1s spectra of PCNT and CNT.



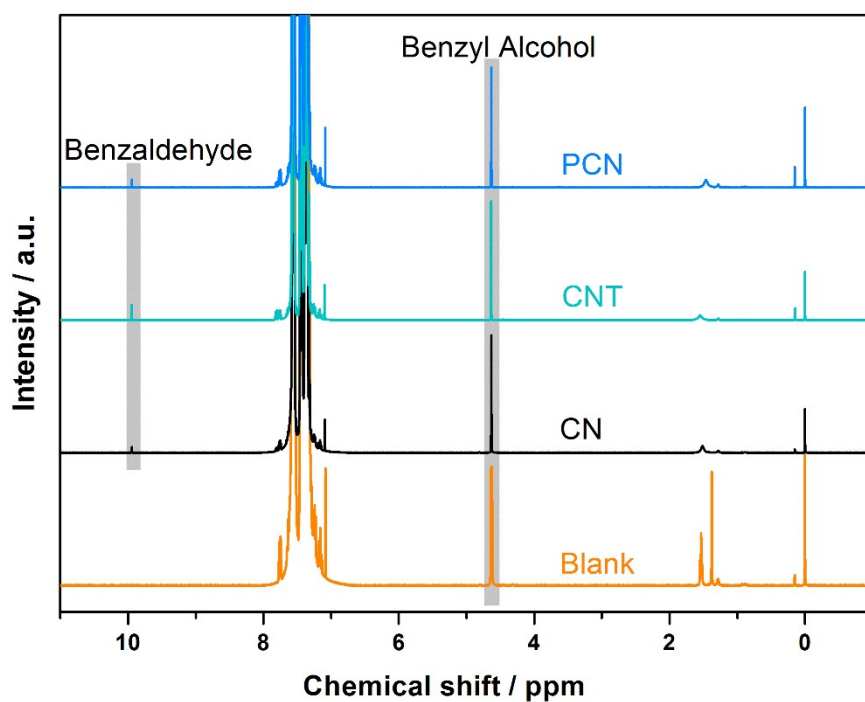
**Figure S3.** (a-d) SEM images of (a) CN, (b) CNT, (c) PCN, and (d) PCNT.



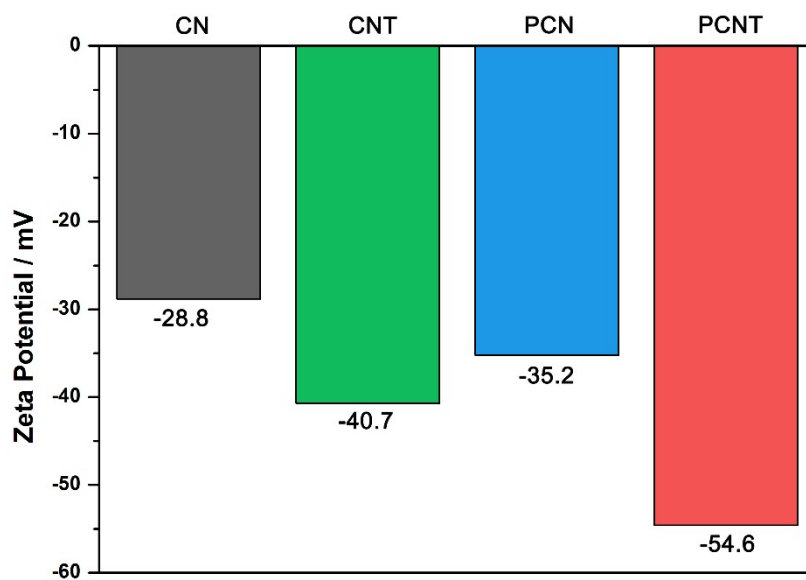
**Figure S4.** TEM image of CN.



**Figure S5.** (a-d) XPS valence band spectra of (a) CN, (b) CNT, (c) PCN, and (d) PCNT.



**Figure S6.** Representative  $^1\text{H}$  NMR spectra of photocatalytic reaction process on CN, CNT, and PCN within 6 h.



**Figure S7.** Zeta Potential of CN, CNT, PCN, and PCNT.